Quantum Chemistry Algorithms: Classical vs Quantum

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Quantum Chemistry on a Quantum Computer

Why?

1. Curiosity

“A Quantum machine may be more efficient at simulating a quantum system than a classical machine.”

Feynman

Quantum Chemistry on a Quantum Computer

Why?

1. Curiosity
2. Difficulty

"The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved."

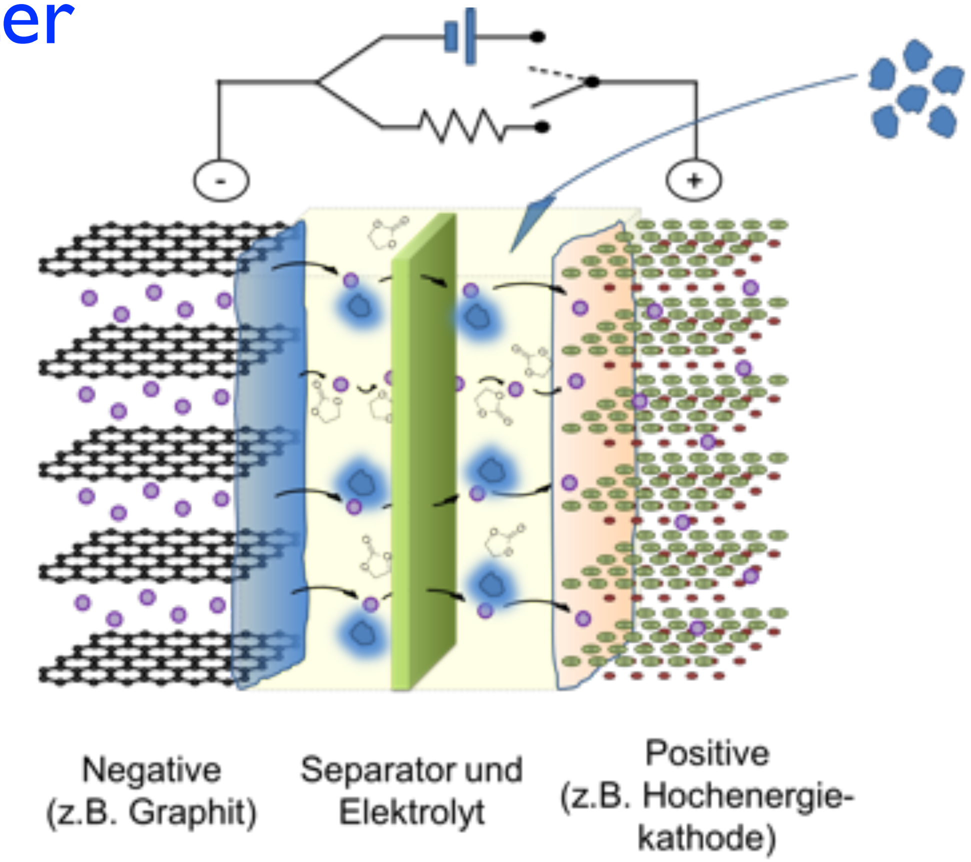
Dirac

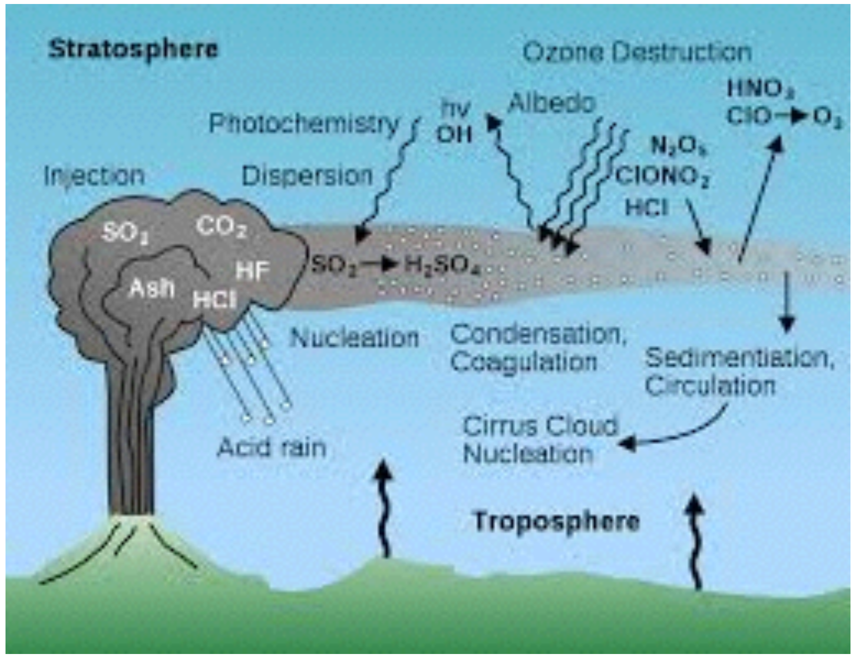
$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$$

Quantum Chemistry on a Quantum Computer

Why?

1. Curiosity
2. Difficulty
3. Importance





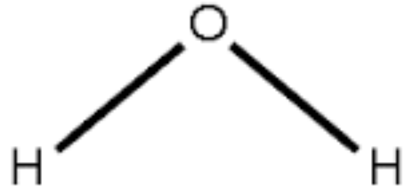
Quantum Chemistry Programs on CPUs (80 and counting)

Package	License[†]	Language	Basis	Periodic[‡]	Mol. mech.	Semi-emp.	HF	Post-HF	DFT	GPU
ABINIT	GPL	Fortran	PW	3d	Yes	No	No	No	Yes	Yes
ACES II	GPL	Fortran	GTO	No	No	No	Yes	Yes	Yes	
ACES III	GPL	Fortran/C++	GTO	No	No	No	Yes	Yes	No	Yes
ADF	Commercial	Fortran	STO	Any	Yes	Yes[4]	Yes	No	Yes	
Atomistix ToolKit (ATK)	Commercial	C++/Python	NAO/EHT	3d[9]	Yes	Yes	No	No	Yes	
BigDFT	GPL	Fortran	Wavelet	Any	Yes	No	Yes	No	Yes	Yes
CADPAC	Academic	Fortran	GTO	No	No	No	Yes	Yes	Yes	
CASINO (QMC)	Academic	Fortran 95	GTO / PW / Spline / Grid / STO	Any	No	No	Yes	Yes	No	
CASTEP	Academic (UK) / Commercial	Fortran	PW	3d	Yes	No	Yes[5]	No	Yes	
CFOUR	Academic	Fortran	GTO	No	No	No	Yes	Yes	No	
COLUMBUS	Academic	Fortran	GTO	No	No	No	Yes	Yes	No	
CONQUEST	Academic	Fortran 90	NAO/Spline	3d	Yes	No	Yes[5]	No	Yes	
CP2K	GPL	Fortran 95	Hybrid GTO / PW	3d	Yes	Yes	Yes	Yes	Yes	Yes
CPMD	Academic	Fortran	PW	3d	Yes	No	Yes	No	Yes	
CRYSTAL	Academic (UK) / Commercial	Fortran	GTO	Any	Yes	No	Yes	Yes[10]	Yes	
DACAPO	GPL ?[1]	Fortran	PW	3d	Yes	No	No	No	Yes	
DALTON	Academic	Fortran	GTO	No	No	No	Yes	Yes	Yes	
DFTB+	Academic / Commercial	Fortran 95	NAO	Any	Yes	Yes	No	No	No	
DFT++	GPL	C++	PW / Wavelet	3d	Yes	No	No	No	Yes	
DIRAC	Academic	Fortran 77, Fortran 90, C	GTO	No	No	No	Yes	Yes	Yes	
DMol3	Commercial	Fortran 90	NAO	Any	No	No	No	No	Yes	
ELK	GPL	Fortran 95	FP-LAPW	3d	No	No	Yes	No	Yes	
Empire	Academic / Commercial	Fortran	Minimal STO	Any	No	Yes	No	No	No	
ErgoSCF	GPL	C++	GTO	No	No	No	Yes	No	Yes	
ERKALE	GPL	C++	GTO	No	No	No	Yes	No	Yes	
EXCITING	GPL	Fortran 95	FP-LAPW	3d	No	No	Yes	No	Yes	
FLEUR	Academic	Fortran 95	FP-(L)APW+lo	3d, 2d, 1d	No	No	Yes	Yes	Yes	
FHI-aims	Commercial	Fortran	NAO	Any	Yes	No	Yes	Yes	Yes	
FreeON	GPL	Fortran 95	GTO	Any	Yes	No	Yes	Yes	Yes	
Firefly / PC GAMESS	Academic	Fortran, C, Assembly	GTO	No	Yes[3]	Yes	Yes	Yes	Yes	Yes
GAMESS (UK)	Academic (UK) / Commercial	Fortran	GTO	No	No	Yes	Yes	Yes	Yes	Yes
GAMESS (US)	Academic	Fortran	GTO	No	Yes[2]	Yes	Yes	Yes	Yes	Yes
Gaussian	Commercial	Fortran	GTO	Any	Yes	Yes	Yes	Yes	Yes	
GPAW	GPL	Python / C	Grid / NAO / PW	3d	Yes	No	Yes[5]	No	Yes	Yes
HiLAPW	Unknown	Unknown	FLAPW	3d	No	No	No	No	Yes	
Jaguar	Commercial	Fortran / C	GTO	No	Yes	No[11]	Yes	Yes	Yes	

The problem

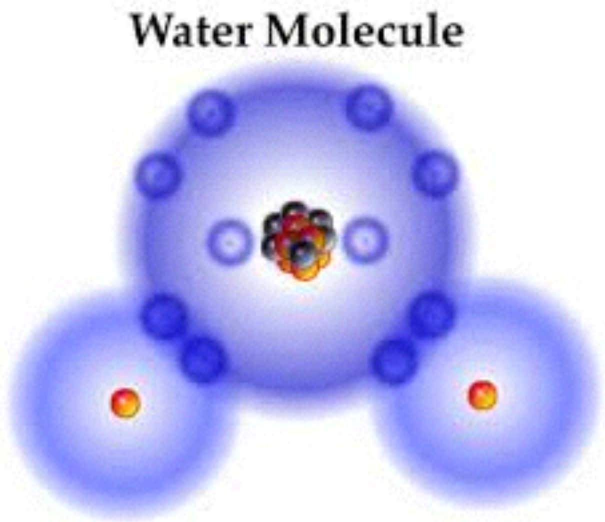
$$\hbar = 4\pi\epsilon_0 = m_e = e = 1$$

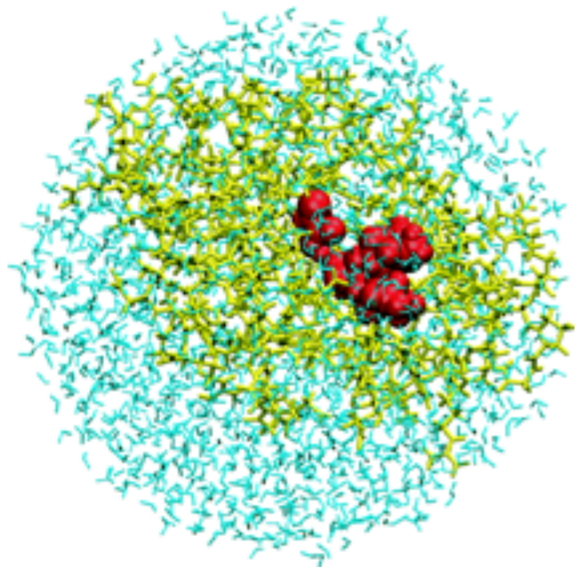
Schrödinger Equation $$i\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$$



$$\hat{H} = -\sum_i \frac{1}{2m_i}\nabla_i^2 + \sum_{i>j}\frac{Z_i Z_j}{r_{ij}}$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n, \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N, t)$$





Water: N = 3 n = 10

Protein: N = 10000 n = 50000

The problem

$$i\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$$

$$\hat{H} = -\sum_i \frac{1}{2m_i}\nabla_i^2 + \sum_{i>j}\frac{Z_i Z_j}{r_{ij}}$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n, \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N, t)$$

↓ some steps

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

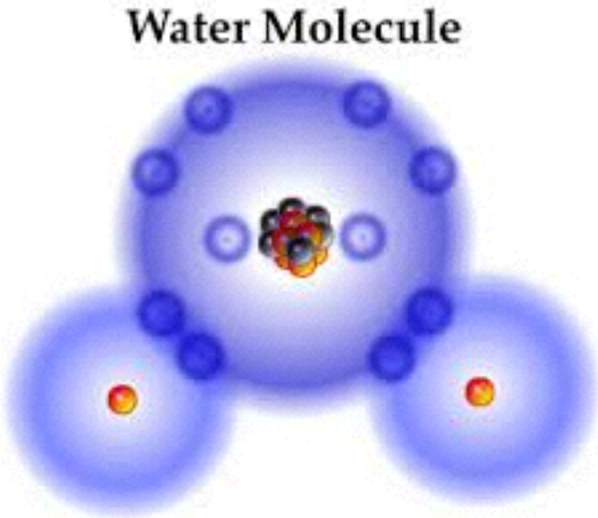
$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \sum_{pqrs} g_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

$$|\psi\rangle = \sum_P C_P |P\rangle$$

The problem

Step 1. Adiabatically separate electronic and nuclear motion

$$\Psi(\mathbf{r}, \mathbf{R}, t) \to \psi_e(\mathbf{r}; \mathbf{R})\psi_n(\mathbf{R}, t)$$



Yields the time-independent Schrödinger Equation for the electrons

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_{I,i} \frac{Z_I}{r_{iI}} + \sum_{i>j} \frac{1}{r_{ij}}$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$$

The problem

Step 2. Select a (finite) basis of 1-p functions (LCAO, PW)

$$\chi_\mu(\mathbf{r}) = x^i y^j z^k e^{-\alpha r^2} \qquad \phi_p(\mathbf{r}) = \sum_\mu c_{\mu p}\chi_\mu(\mathbf{r})$$

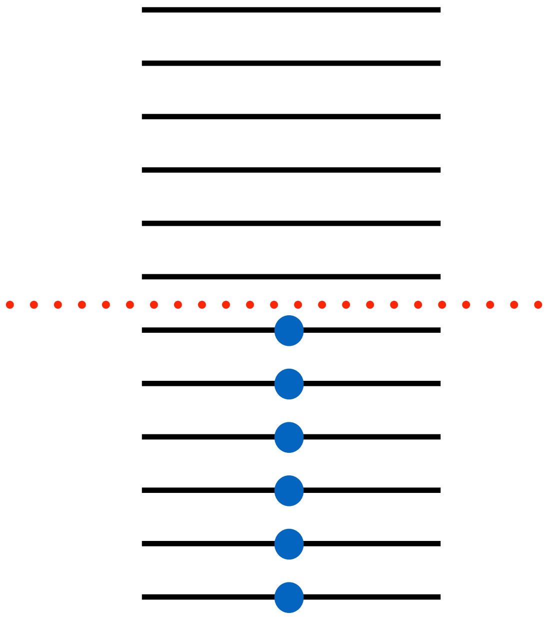
- Mean field approximation (independent particle model)

$$\psi_{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = \hat{\mathcal{A}} \prod_i \phi_i(\mathbf{r}_i)$$

$$\hat{F}\phi_p(\mathbf{r}) = \varepsilon_p \phi_p(\mathbf{r})$$

Defines a set of one-particle states

and an n-particle Hilbert space



$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \sum_{pqrs} g_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

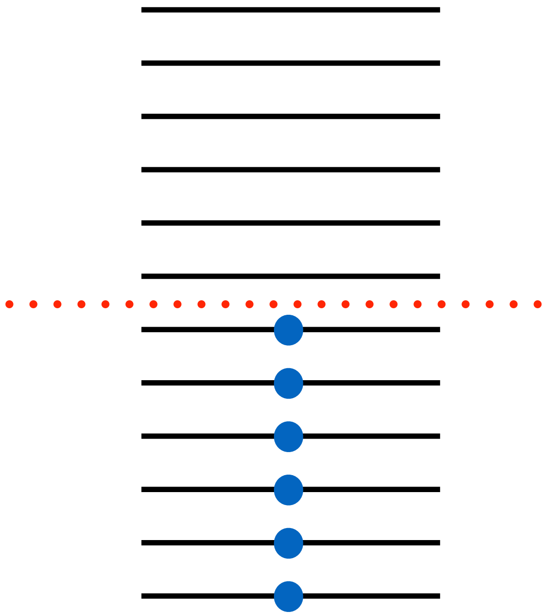
The problem

Step 3. Find the eigenstates

$$\hat{H}|\psi\rangle = E|\psi\rangle \qquad \hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \sum_{pqrs} g_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

Dimension of n-p Hilbert space is combinatorial in the number of electrons (n) and available1-p states (m)

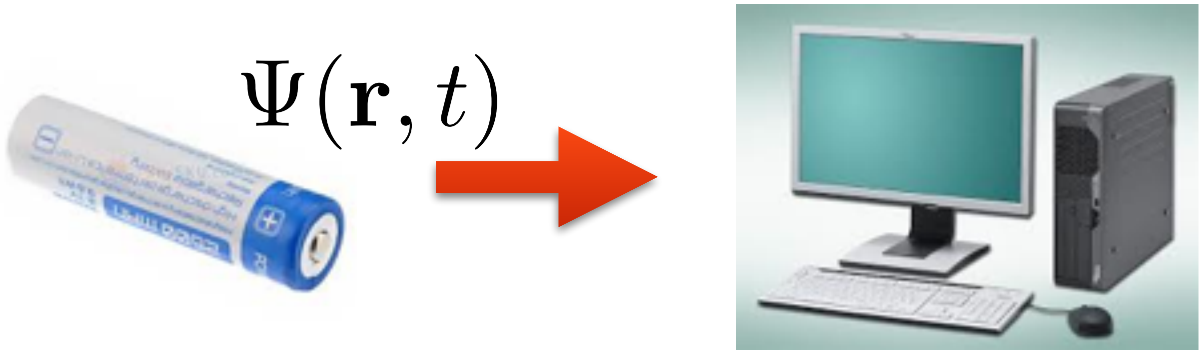
$$|\psi\rangle = \sum_P C_P |P\rangle \qquad \binom{m}{n}$$



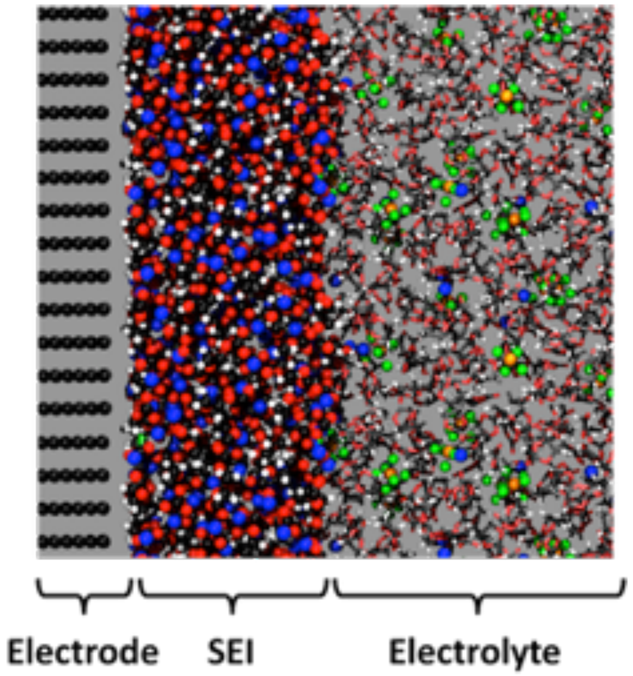
Water: m = 30 n = 10 : 10^{10}

Protein: m = 150000 n = 50000 : 10^{10000}

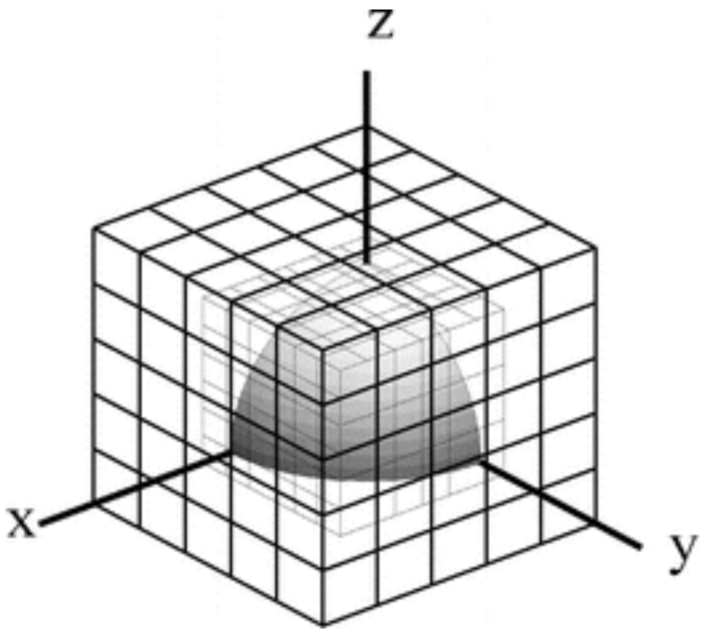
Three layers of approximation


$\Psi(\mathbf{r}, t)$

Simulation
window



1-p Representation
cut-off



basis set
incompleteness

n-p Representation
cut-off

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

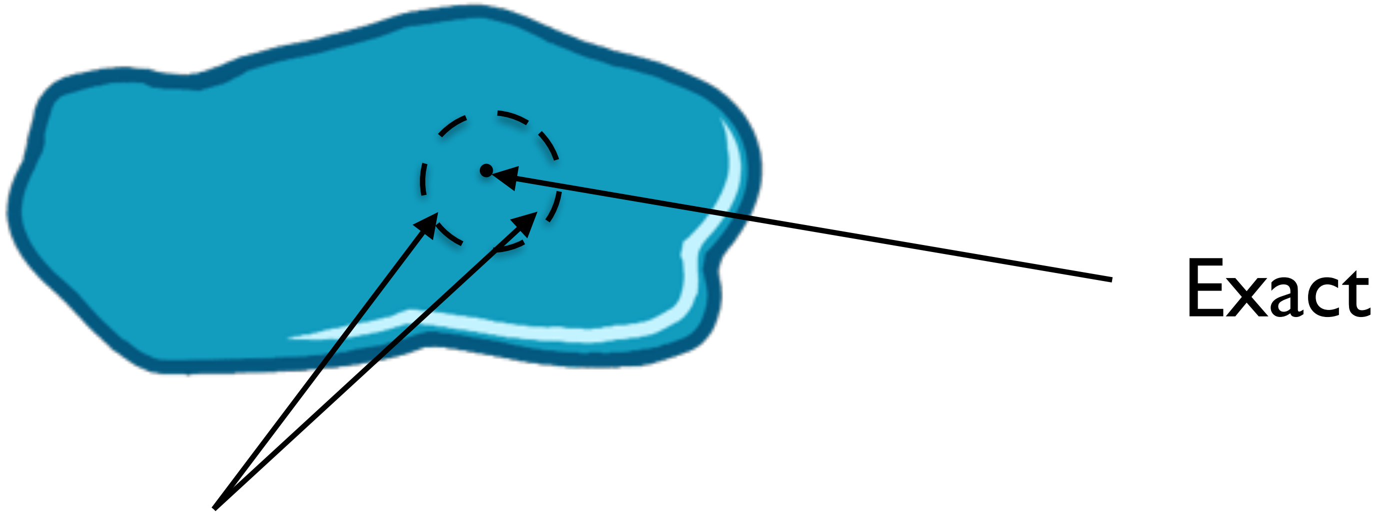
$$|\psi\rangle = \sum_P C_P|P\rangle$$

polynomial number
of parameters

The problem

Step 3. Find approximations to the eigenstates

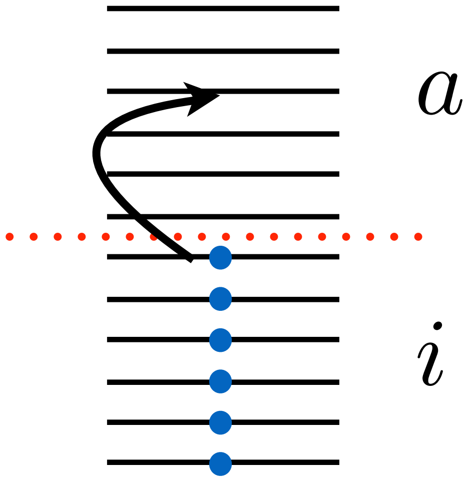
$$\hat{H}|\psi\rangle = E|\psi\rangle \qquad \hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \sum_{pqrs} g_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$



- $E + \epsilon$ is acceptable
- Provided $\epsilon/n <$ “Chemical accuracy”

Classical Algorithm 1: Coupled Cluster

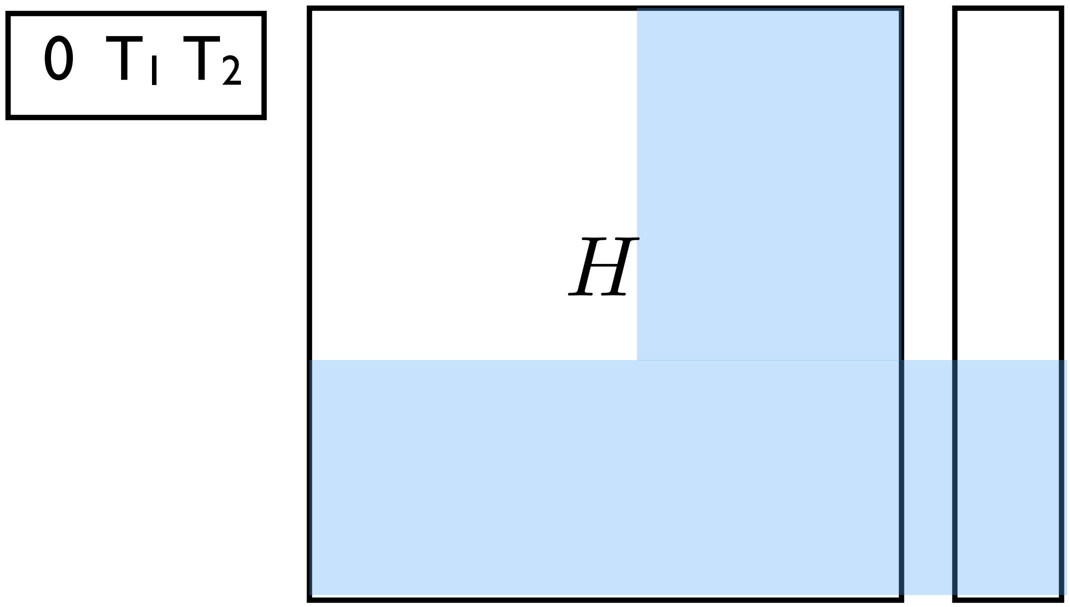
$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \sum_{pqrs} g_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$



- Factorised many-body expansion

$$|\psi\rangle = e^T |0\rangle \qquad T = \sum_{ai} t_i^a a_a^\dagger a_i + \sum_{abij} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

- Obtain energy and coefficients via projection (like PT)

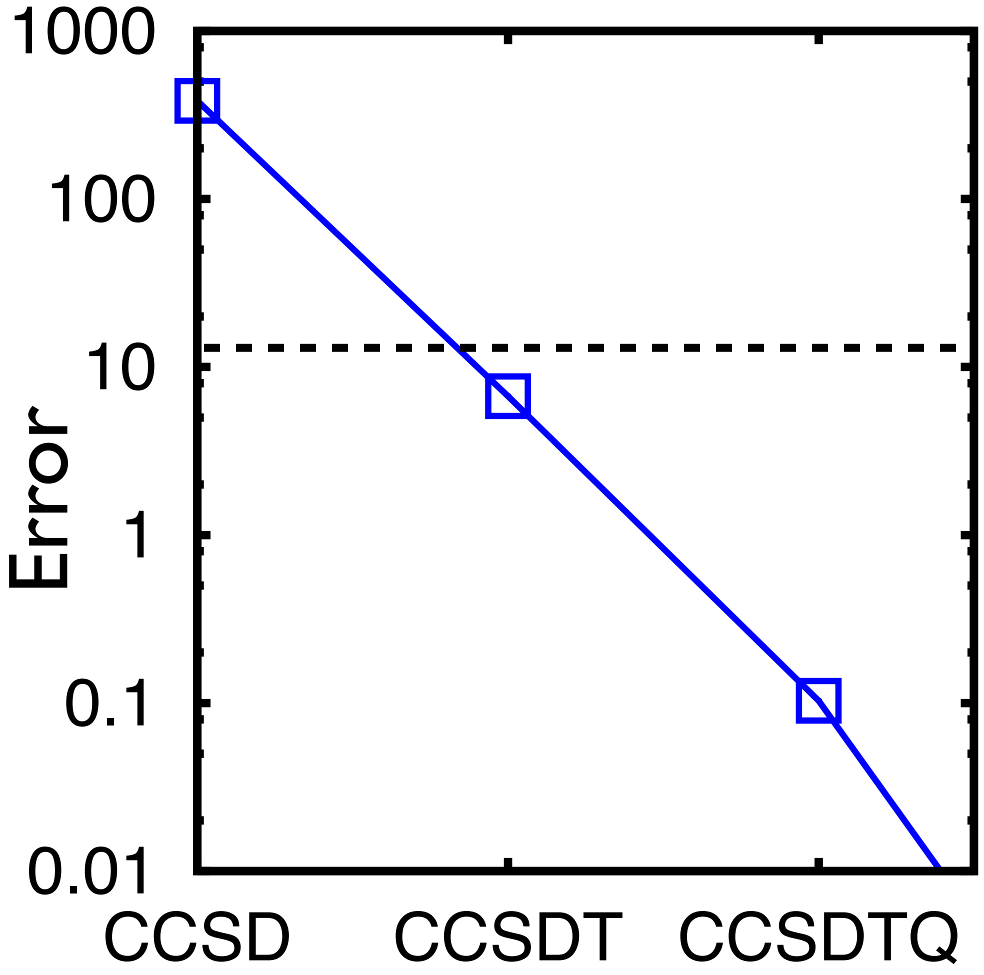


$$n^2 m^4$$

Classical Algorithm 1: Coupled Cluster

For many cases, convergence with respect to truncation of many-body expansion is near exponential

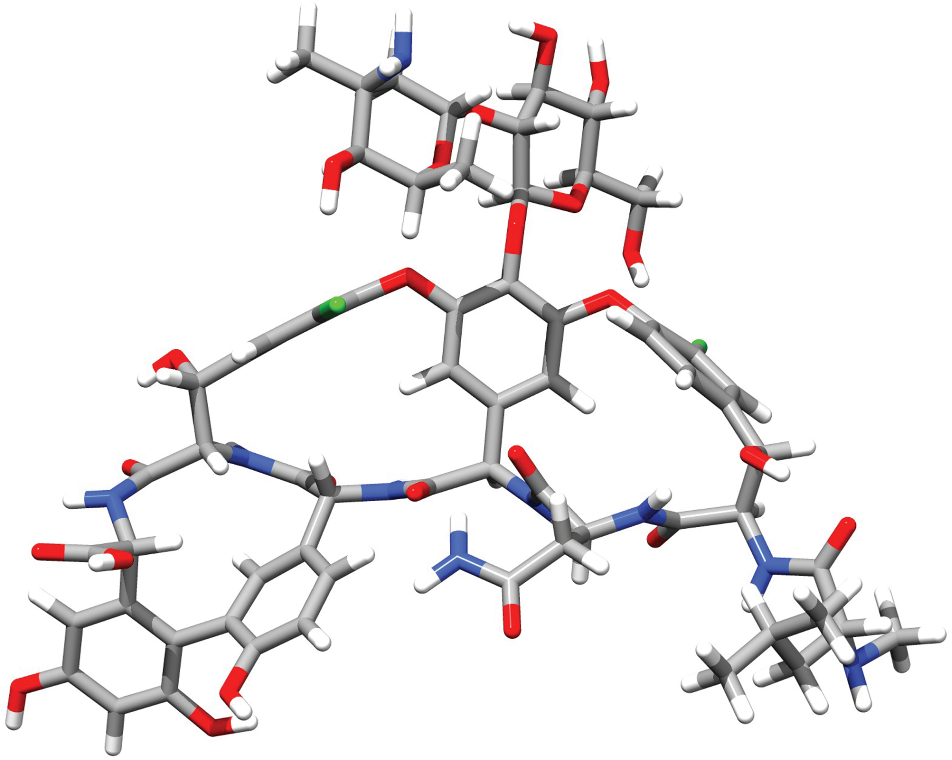
$$|\psi\rangle = e^{T_1+T_2+T_3+\dots}|0\rangle$$



chemical accuracy

Coupled Cluster State of the art

- For insulators, the interactions are short range:
  polynomial number of parameters and operations: $O(n)$



$m > 8800$

$n > 900$

$N > 450$

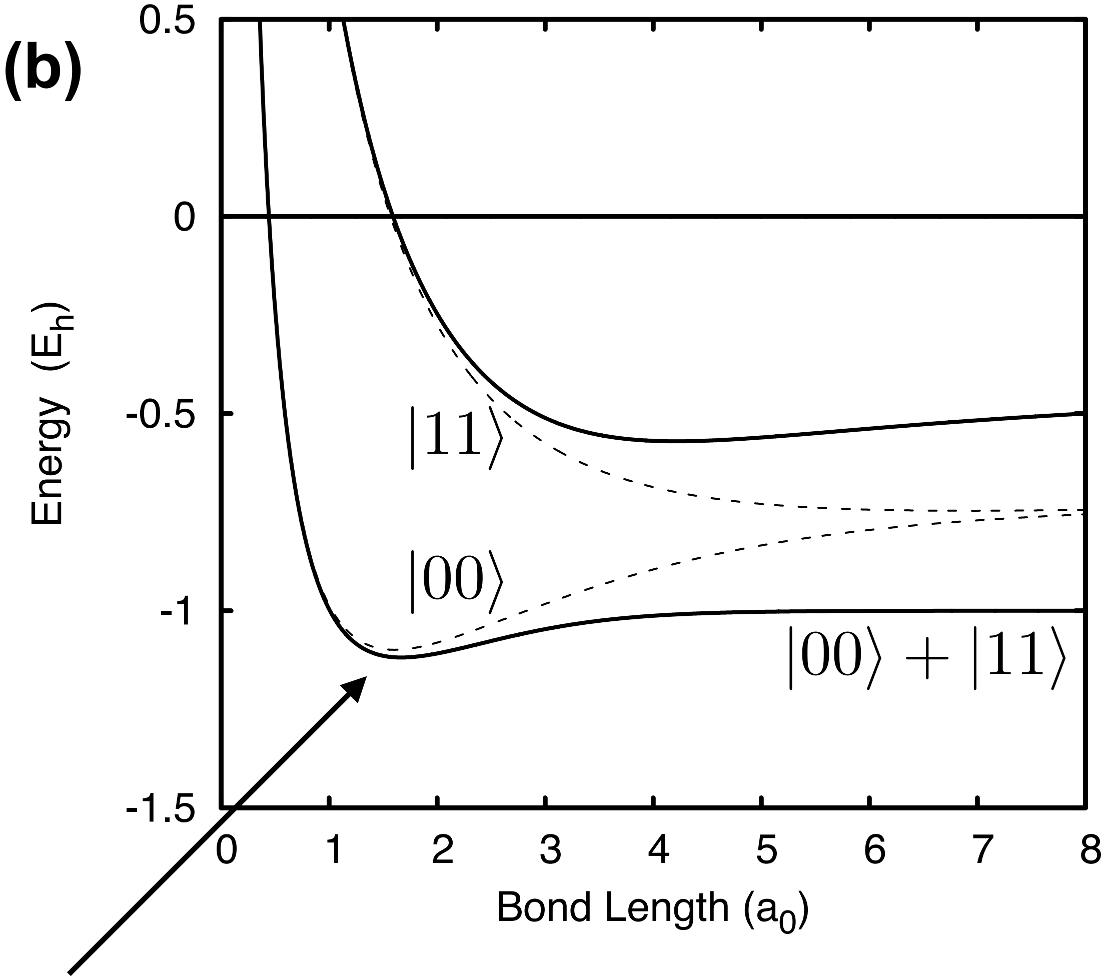
time 10^6 seconds

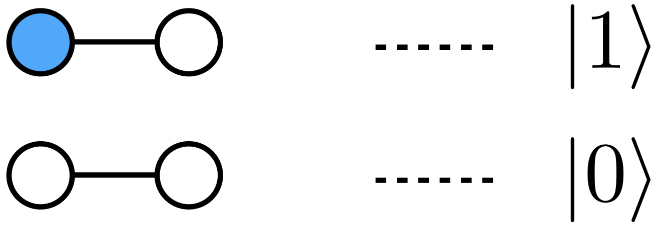
(2 weeks, 1 CPU)

Chemical accuracy for e.g. binding energies

Coupled Cluster success and failure

Simple example of H_2 with varying bond length





Works well

Fails

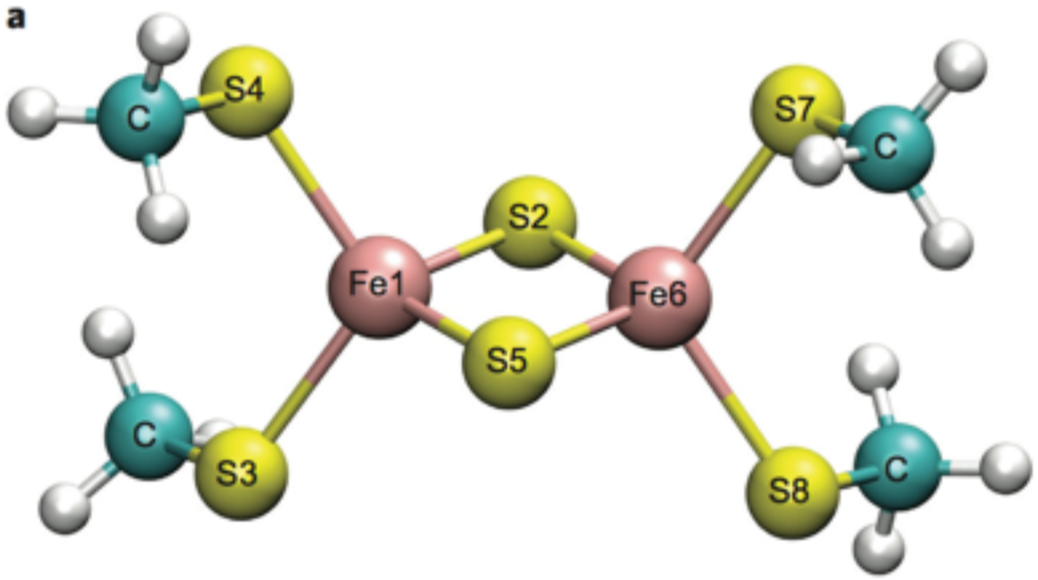
Classical Algorithm 2: DMRG

Tensor train factorisation of the CI vector

$$C_{DMRG}^{n_1 n_2 n_3 n_4} = \sum_{i_1 i_2 i_3 \ldots}^{M} A_{i_1}^{n_1} A_{i_1 i_2}^{n_2} A_{i_2 i_3}^{n_3} A_{i_3 i_4 \ldots}^{n_4}$$

State-of-the-art

m = 64 n = 30 : 10^{17}



Classical Algorithm 3: FCI-QMC

A stochastic realisation of the imaginary-time Schrödinger Equation in n-particle Hilbert-space

$$i\frac{\partial \Psi}{\partial t} = \hat{H}\Psi \qquad \longrightarrow \qquad \frac{\partial \Psi}{\partial \tau} = -\hat{H}\Psi$$

The CI coefficients are represented through a population of walkers in Hilbert space. After reaching steady state, energies and properties are extracted through time-averaging

$$-\frac{\partial C_P}{\partial \tau} = (H_{PP} - E)C_P + \sum_{Q \neq P} H_{PQ} C_Q$$

State-of-the-art : > 10^{20}

Classical Algorithm 4: Density Functional Theory

There is an existence proof that there is a one-to-one mapping between the wave function and the electron density

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) \leftrightarrow \rho(\mathbf{r})$$

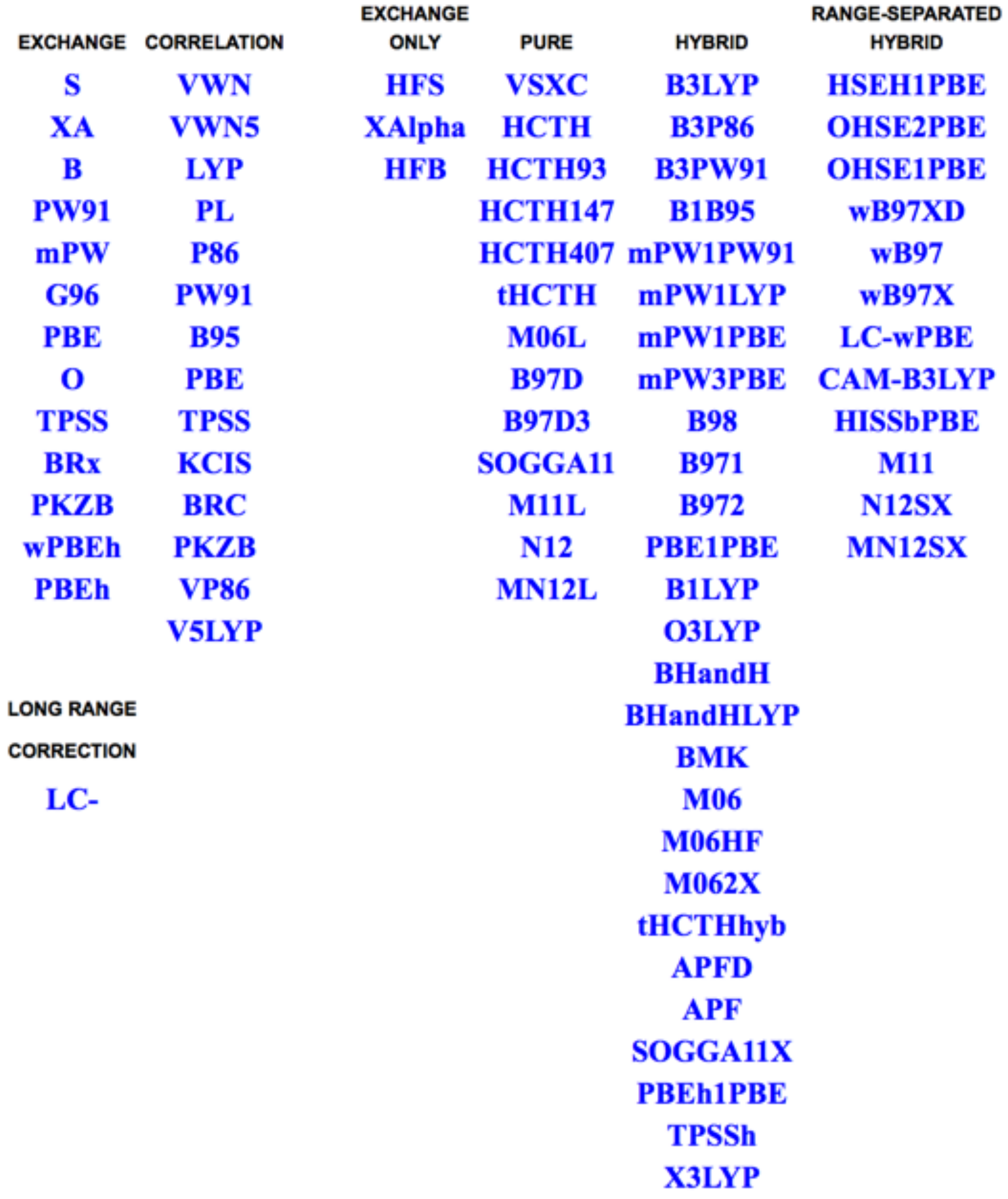
$$\min_{\rho} E[\rho]$$ for n-representable densities

Kohn-Sham: search over non-interacting mean-field states

$$\hat{\mathcal{A}} \prod_i \phi_i(\mathbf{r}_i) \rightarrow \rho(\mathbf{r})$$

$$E[\rho] = T_s + V[\rho] + J[\rho] + V_{xc}[\rho]$$

Approximate Density Functionals in G09



EXCHANGE

S
XA
B
PW91
mPW
G96
PBE
O
TPSS
BRx
PKZB
wPBEh
PBEh

CORRELATION

VWN
VWN5
LYP
PL
P86
PW91
B95
PBE
TPSS
KCIS
BRC
PKZB
VP86
V5LYP

LONG RANGE CORRECTION

LC-

EXCHANGE ONLY

HFS
XAlpha
HFB

PURE

VSXC
HCTH
HCTH93
HCTH147
HCTH407
tHCTH
M06L
B97D
B97D3
SOGGA11
M11L
N12
MN12L

HYBRID

B3LYP
B3P86
B3PW91
B1B95
mPW1PW91
mPW1LYP
mPW1PBE
mPW3PBE
B98
B971
B972
PBE1PBE
B1LYP
O3LYP
BHandH
BHandHLYP
BMK
M06
M06HF
M062X
tHCTHhyb
APFD
APF
SOGGA11X
PBEh1PBE
TPSSh
X3LYP

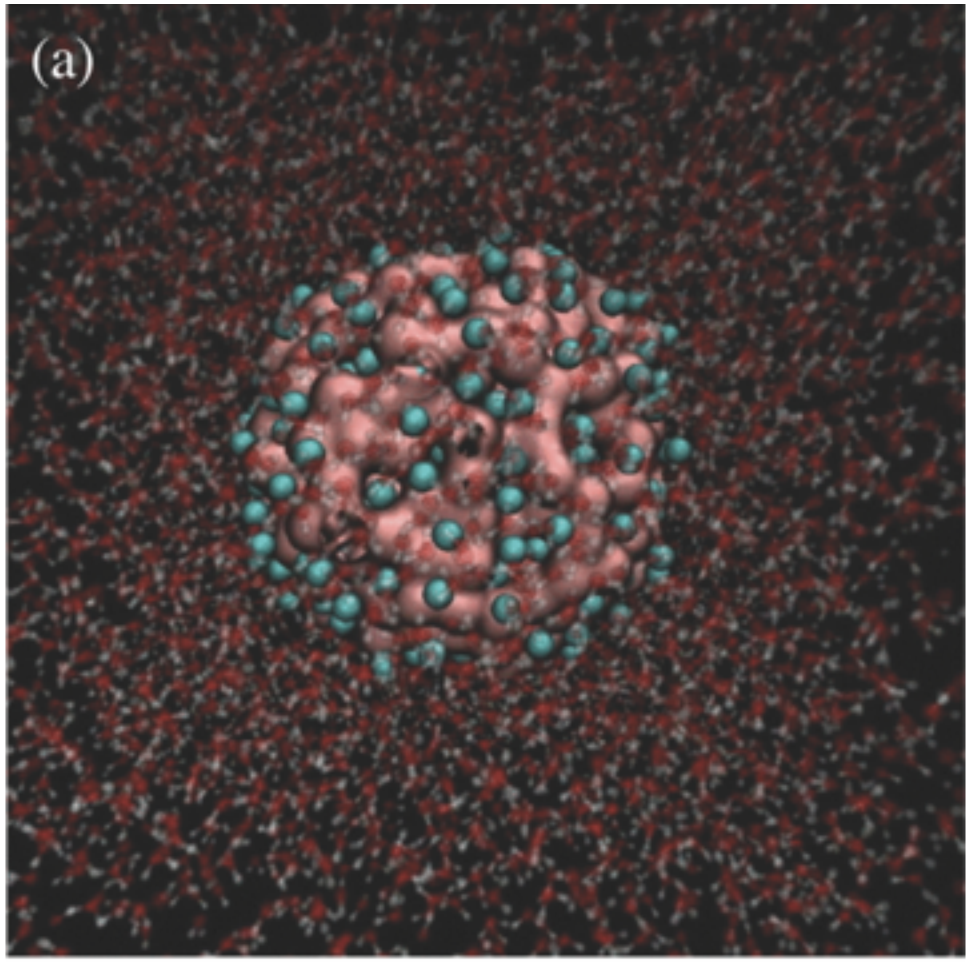
RANGE-SEPARATED HYBRID

HSEH1PBE
OHSE2PBE
OHSE1PBE
wB97XD
wB97
wB97X
LC-wPBE
CAM-B3LYP
HISSbPBE
M11
N12SX
MN12SX

State-of-the-art for DFT

Accuracy - twice “Chemical Accuracy” if the molecule under investigation resembles those the functionals were parameterised to get right. Else …

(Important, but shrinking, class of problems for which DFT fails)



N = 16000

m = 100000

n = 50000

1000 time steps

Blue Gene/Q

Summary

For a wide class of molecules, the electronic structure of the undistorted ground state is relatively easy. Weakly correlated.

DFT and CCSD(T) hit different sweet spots of accuracy vs cost

An important class of systems have difficult electronic structure, usually characterised by many degenerate or near degenerate states and a poor mean field solution. Strongly correlated.

We don't know how to solve these problems efficiently and reliably.

Quantum Chemistry on a Quantum Computer

Exploit the mapping of Fermionic creation and annihilation operators onto qubit operations

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \sum_{pqrs} g_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

Unitary-type operations can be used to prepare a state, perform QFT, and evolve a state according to a Hamiltonian

$$|\psi\rangle = U|0\rangle \qquad\qquad e^{i\hat{H}t}|\psi\rangle$$

Trotter expansion makes it possible to decompose general angle unitaries from $e^{i\hat{H}t}$ into a sequence of local angle unitaries.

Quantum Algorithm 1: Phase Estimation

Prepare

$|\psi\rangle = U|0\rangle$

QFT

E

Requires that $|\psi\rangle$ has a large overlap with the true eigenstate

For the easy cases, where CC works, this is probably possible

Open question: How to prepare good states for hard cases?

Prepare

$|0\rangle$

Adiabatic map

$e^{i((1-t)\hat{F}+t\hat{H})}|0\rangle$

QFT

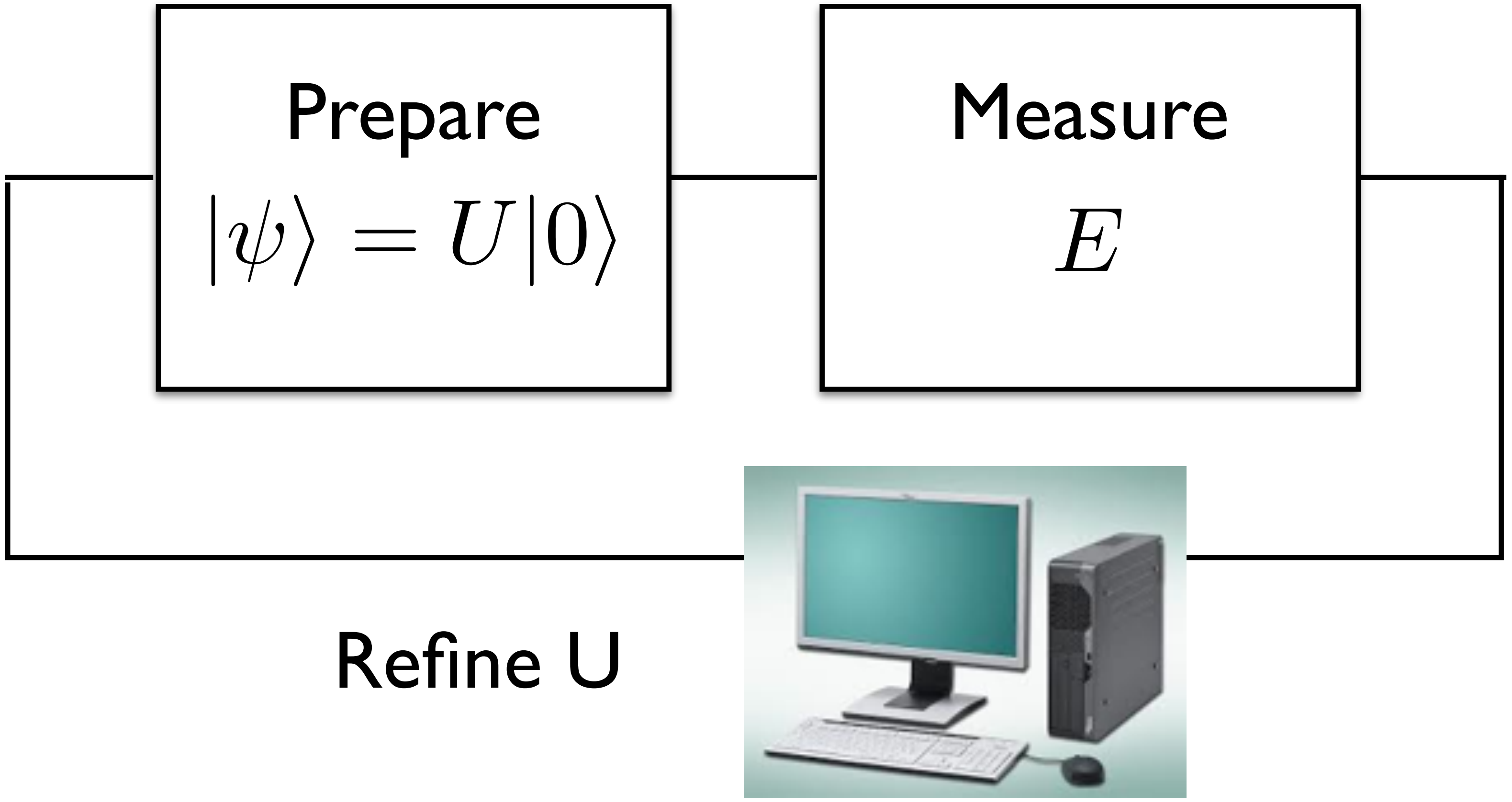
E

Quantum Algorithm 2: Variational Approach

Decompose the Hamiltonian into a sum of unitary operations

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \sum_{pqrs} g_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

$$= \sum_i c_i U_i$$



Prepare

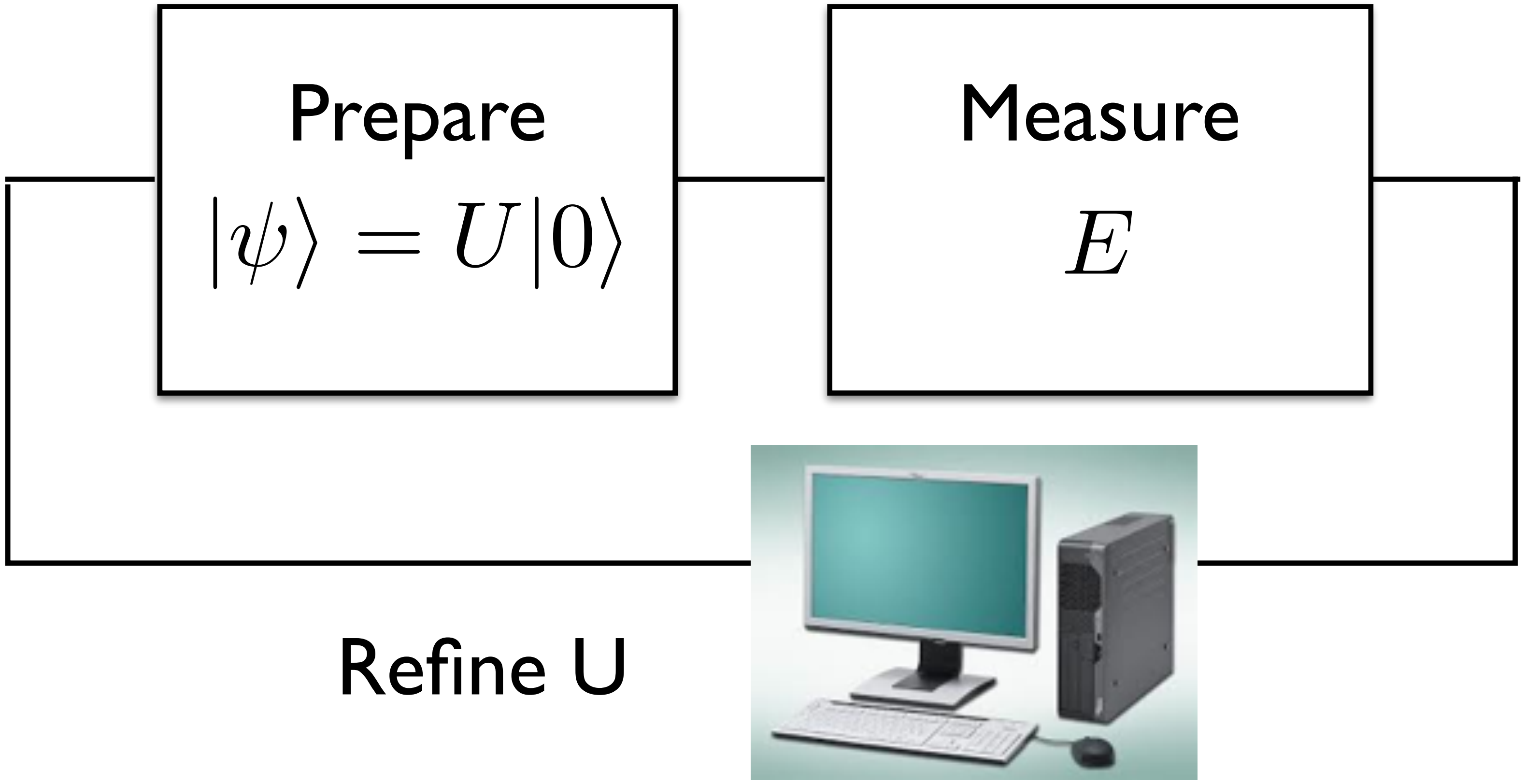
$|\psi\rangle = U|0\rangle$

Measure

E

Refine U

Quantum Algorithm 2: Variational Approach



Prepare

$|\psi\rangle = U|0\rangle$

Measure

E

Refine U

We will only have access to a limited space of unitaries

$$U = e^{\hat{T} - \hat{T}^\dagger}$$

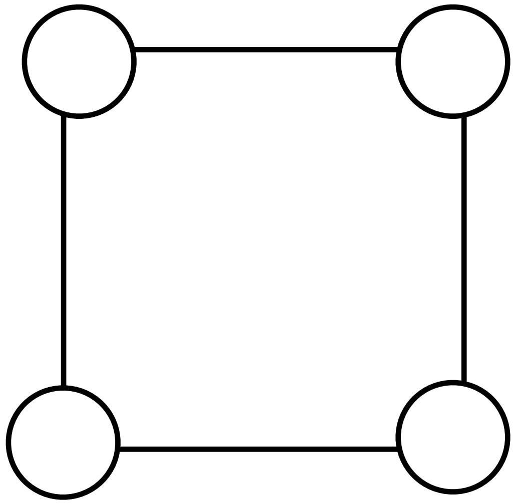
Questions:

Is unitary truncated coupled cluster better than regular?

How easy or hard is the refinement of U?

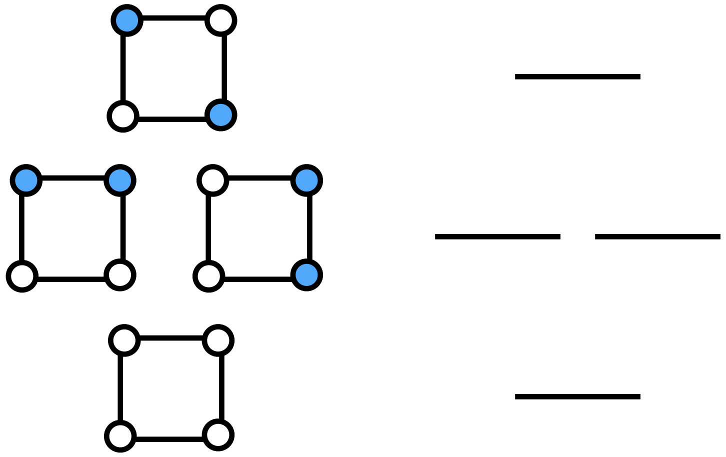
Quantum Algorithm 2: Variational Approach

Numerical experiments for a 1-d periodic Hubbard Hamiltonian



$$\hat{H} = -t \sum_{\langle i,j\rangle \sigma} a^{\dagger}_{i\sigma} a_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

4 1-particle states for each spin



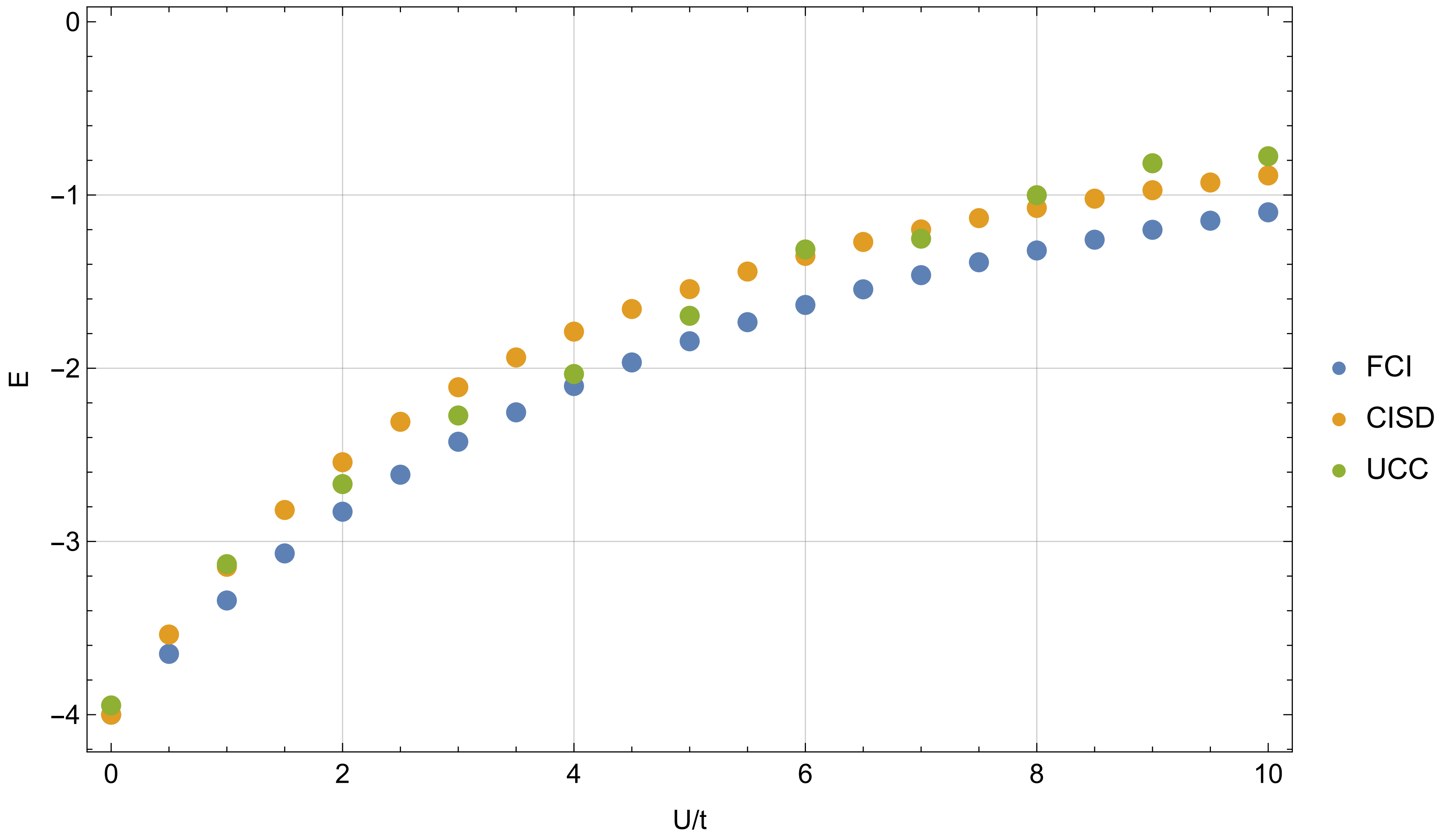
Half-filled case:

2 up spin particles, two down spin particles: 36 states

Quantum Algorithm 2: Variational Approach

Numerical experiments for a 1-d periodic Hubbard Hamiltonian

$$|\psi\rangle = e^{\hat{T}-\hat{T}^\dagger}|0\rangle \qquad T = \sum_{ai} t_i^a a_a^\dagger a_i + \sum_{abij} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$



Summary

Classical algorithms are efficient when the electronic structure is well approximated by one occupation number state

Classical algorithms struggle when many occupation number states are required for a qualitatively correct ground state. This is where quantum algorithms will probably have the biggest impact.

This situation occurs in e.g. superconducting materials and clusters of transition metal atoms in the body

Many important topics have not been mentioned:

- Excited states for Fermionic systems
- Bosonic Hamiltonians for QM of nuclei